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Appl. No.	10/045,948
Applicant	Zemanian, et al.
Filed	10/26/2001
Title	MONOLAYER COATED AEROGELS AND METHOD OF MAKING
TC/A.U.	1712
Examiner	Lovering, Richard D.
Docket No.	E-13260

Mail Stop Non-Fee Amendment
Commissioner for Patents
P.O. Box 1450
Alexandria, VA 22313-1450

Rule 132 AFFIDAVIT of Dr. WILLIAM D. SAMUELS

I, WILLIAM D. SAMUELS, hereby to state and affirm as follows:

I was awarded a B.A. degree in Chemistry from Coe College in 1974, and completed my Ph.D. in Organic Chemistry at the Georgia Institute of Technology in 1980. From 1984-1987 I served a NORCUS Postdoctoral Fellowship at the Department of Energy's Pacific Northwest National Laboratory (PNNL) in Richland, Washington. Beginning in 1987, I accepted a full time position at PNNL, and I have been continuously employed at PNNL ever since. I am currently a Senior Research Scientist in the Molecular and Solid State Research Group. In addition to my work at PNNL, I have accepted appointment as an adjunct professor at the Washington State University-Tri-Cities in Chemistry beginning in 2000 and at Clemson University in Materials and Ceramic Sciences beginning in 1997.

My major research has been in the design, synthesis, isolation, and characterization of model phosphazene polymers, has been the major research. The synthesis of these polymers utilizes air sensitive chemical techniques. Polyphosphazenes are a series of short organic moieties attached onto an inorganic backbone. The uniqueness of these polymers is the ability to drastically change the physical and chemical properties of these materials. Initial interest in these polymers was for the study of the chemical interaction of polymers with metal oxides during the formation of ceramic greenbodies and subsequent densification. The incorporation of polyphosphazenes and other polymers into a silicone dioxide or alkaline metal and zinc pyrophosphate matrix has been examined for utility as coatings, membranes, and for other enhanced physical properties. Further work with the polyphosphazenes has led to applications of these materials into separation membranes, optical materials, sensors, and recently in reabsorable biomaterials. Composite materials with chemically defined interfacial properties have

also become a major research area. This work has included fiberglass, carbon fiber and composites from waste fiber sources. The work was initiated to improve the mechanical, environmental, physical properties of the composites.
Other research activities in the 1990's have also included investigations into the chemical and radiological Aging of organic components thought to be present in the Organic Underground Storage Tanks (UST) at the Hanford Complex. The organic and inorganic soup that compromises the UST mixtures offers multi opportunities for application of basic organic and inorganic analysis. Relative rates of Aging and G values have been derived for individual organic species. These studies have looked at the generation of non-compressible gases.

A summary of my publications, patents, technical reports, and presentations is set forth below.

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I have reviewed the above-captioned patent application, as well as United States Patent No. 3,920,865 to Läufer et al. and United States Patent No. 5,716,705 to Wirth et al. In comparing the aforementioned patents to the claims of above-captioned patent application, I would offer the following observations:

With respect to the Läufer patent, it is plain that the method taught by Läufer will not produce a monolayer coating, as is required by claims 1-10 of the above-captioned patent application, and as is accomplished by the method taught in claims 11-25 of the above-captioned patent application. Läufer discloses a method of rendering highly dispersed metal or metalloid oxides hydrophobic by exposing these substrates to organopolysiloxanes. While Läufer only provides examples utilizing octamethyltetrasilooxane, he broadly describes hydophobizing agents as including alkyl or aryl or mixed alkyl-aryl halogenosilanes, preferring dimethyldichlorosilane, and including the corresponding esters of the silanes.

In all cases the coverage of the substrate with these materials will not produce a monolayer.

With respect to the cyclic octamethyltetrasilooxane used in Läufer's examples, the opening of the cyclic chains, which is necessary for the chains to bond to the substrate, will produce a ring opening polymerization catalyst, resulting in a living polymer and resultant polymerization that will not be limited to the surface of the substrate.

With respect to the remainder of the materials disclosed by Läufer, a monolayer will also not be formed. In cases such as the di-chloro and di-ester compounds, these compounds will polymerize in a manner similar to the cyclics described above, although by a slightly different mechanism. In the remaining cases, a monolayer will not form because the distribution of varying chain lengths will cause the entrapment of excess reagent.

The failure of these materials to form monolayers is well understood, as the reactions described above are well documented in the scientific literature. Further, these reactions are well understood by those studying the problem solved by the above captioned patent application. Examples of publications demonstrating this behavior include the following, which is by no means an exhaustive listing:

Synthesis of Polymethyl(trimethylsiloxy)siloxane by Anionic Ring-Opening Polymerization of 1,3,5-Trimethyl-1,3,5-tris(trimethylsiloxy)cyclotrisiloxane Cai, G. P.; Weber, W. P.; Macromolecules; (Article); 2000; 33(17); 6310-6314.

Microstructure of the Copolymer Chain Generated by Anionic Ring-Opening Polymerization of a Model Cyclotrisiloxane with Mixed Siloxane Units1 Cypryk, M.; Kazmierski, K.; Fortuniak, W.; Chojnowski, J.; Macromolecules; (Article); 2000; 33(5); 1536-1545.

Preparation and Orthogonal Polymerizations of 1-Hydrido-1-vinyldimethylsiloxy-3,3,5,5-tetramethylcyclotrisiloxane Paulasaari, J. K.; Weber, W. P.; Macromolecules; (Article); 1999; 32(16); 5217-5221.

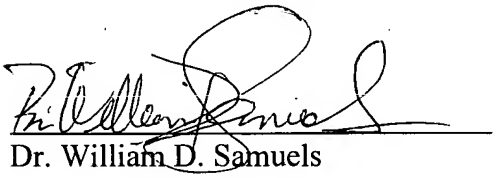
1,1,3,3,5,5,7,7-Octaphenyl-1,3,5,7-tetrasiloxane-1,7-diol and Its Organotin Derivatives. Model Compounds for Diphenylsiloxane Polymer Beckmann, J.; Jurkschat, K.; Muller, D.; Rabe, S.; Schurmann, M.; Organometallics; (Article); 1999; 18(12); 2326-2330.

Silica-Dimethylsiloxane Hybrids-Non-Hydrolytic Sol-Gel Synthesis and Characterization by NMR Spectroscopy Apperley, D.; Hay, J. N.; Raval, H. M.; Chem. Mater.; (Article); 2002; 14(3); 983-988.

Synthesis of Organic-Inorganic Hybrids via the Non-hydrolytic Sol-Gel Process Hay, J. N.; Raval, H. M.; Chem. Mater.; (Review); 2001; 13(10); 3396-3403.

With respect to the Wirth et al. patent, I note that while Wirth et al. do describe a method for forming monolayer coatings, Wirth et al. does not use their method to form these coatings on aerogels. Also, Wirth et al.'s method forms the monolayer coatings using a liquid phase. Unfortunately, as is well understood by those working with aerogels, the use of a liquid phase in combination with aerogels will cause the structure of the aerogels to collapse. Thus, while Wirth et al. describe a useful method for forming a monolayer on parts such as glassware, the Wirth et al. method would not be successful for coating aerogels, as contemplated in the above referenced patent application.

In summary, based on my experience in the field of polymer chemistry, neither the Wirth et al. patent nor the Läufer et al. patent, either alone or in combination, describe or suggest a workable method that would result in aerogels having monolayer coatings.



Dr. William D. Samuels

June 30, 2003
date